STABILITY AND CONFIGURATION OF VINYL ALCOHOLS

BY

EVERETT WILLIAM MAYNERT

Sc.B., Brown University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1945

URBANA, ILLINOIS

1945

STABILITY AND CONFIGURATION OF VINYL ALCOHOLS

BY

EVERETT WILLIAM MAYNERT

Sc.B., Brown University, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1945

URBANA, ILLINOIS

1945

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Reynold C. Fuson for his advice and suggestions during the course of this investigation.

STABILITY AND CONFIGURATION OF VINYL ALCOHOLS

INTRODUCTION

A survey of the facts available at present indicates that vinyl alcohols which contain only hydrocarbon substituents may be stabilized by resonance alone, by steric hindrance alone or by a proper combination of these. Other factors such as the interaction of the hydrogen of the hydroxyl group with the highly electronegative carbon 1 of a mesityl radical on the *beta* carbon atom of the vinyl alcohol structure may also operate to enhance stability.[1]

A number of stable aldehyde enols in which one or both of the aryl groups are hindering radicals, such as mesityl, have been prepared recently.[2,3,4,5] These compounds have been reported to show no tendency to rearrange to the corresponding aldehydes. Attempts to prepare the aldehydes by isomerization[2,6] and by direct synthesis[5,6,7] have failed. Diphenylacetaldehyde, on the other hand, does not form a stable enol. In an effort to prepare a vinyl alcohol for which the tautomeric diarylacetaldehyde can be isolated, work was directed toward the preparation of vinyl alcohols in which it is believed the hindrance is less than in 2-mesityl-2-phenylvinyl alcohol. One attractive scheme for decreasing the hindrance was to introduce halogen atoms into the aromatic rings.[9,10]

The aldehyde enols should exhibit *cis-trans* isomerism, but in no case has there been any evidence for more than one configuration. Since geometrical isomerism is more likely to be observed in compounds in which the groups are not too dissimilar, it was decided to prepare 2-isoduryl-2-mesitylvinyl alcohol.

DISCUSSION OF RESULTS

The aldehyde enols were synthesized by adaptations of two methods used by Shenk.[5] The first involves the cleavage of enol peroxides and the second the reduction of ketenes with a Grignard reagent.

2-(*p*-Chlorophenyl)2-mesitylvinyl alcohol was prepared in low yield by the thermal cleavage of 1,3-dimesityl-3(*p*-chloro-

phenyl)1-propen-1-ol peroxide. The peroxide was obtained by the addition of mesitylmagnesium bromide to *p*-chlorobenzalacetomesitylene followed by treatment of the enol with oxygen. 1,3-Dimesityl-3(*p*-bromophenyl)1-propen-1-ol peroxide also was synthesized, but the vinyl alcohol could not be isolated from the cleavage products.

Bromomesitylphenylacetic acid was prepared by the treatment of mandelic acid with bromomesitylene in the presence of stannic chloride and also by the bromination of mesitylphenylacetic acid. The acid was converted to the corresponding ketene by the action of thionyl chloride and pyridine. 2-Bromomesityl-2-phenylvinyl alcohol was obtained by the reduction of the ketene with cyclohexylmagnesium chloride and with *t*-butylmagnesium chloride. The latter Grignard reagent also was used with excellent results for the reduction of dimesitylketene, mesitylphenylketene and durylphenylketene to the corresponding vinyl alcohols.

Although it appeared certain that mesitylphenylacetaldehyde and dimesitylacetaldehyde enolize spontaneously to give stable vinyl alcohols, there was some doubt as to whether or not the vinyl alcohols were in equilibrium with the aldehydes in solution. This question was answered by treating solutions of the vinyl alcohols with semicarbazide. 2-Mesityl-2-phenylvinyl alcohol was converted to a semicarbazone, but 2,2-dimesitylvinyl alcohol was recovered unchanged. The formation of the semicarbazone furnishes the first evidence for the existence of a diarylacetaldehyde which is isomeric with a stable vinyl alcohol and may provide an explanation for the fact that none of the aldehyde enols containing only one hindering radical have been isolated in more than one configuration. The failure of 2,2-dimesitylvinyl alcohol to form a semicarbazone seems to imply that aldehyde enols with two hindering radicals are completely enolic and, if unsymmetrically substituted, should be expected to exhibit geometrical isomerism.

Isodurylmesitylacetic acid was prepared by the treatment of isodurylglycolic acid with an equimolecular amount of mesitylene and of mesitylglycolic acid with an equimolecular amount of isodurene; both reactions were carried out in carbon disulfide

solution in the presence of stannic chloride. The treatment of isodurylglycolic acid with an excess of mesitylene in the presence of stannic chloride or hydrofluoric acid gave a remarkable result; the product was dimesitylacetic acid. An experiment in which mesitylglycolic acid was treated with an excess of isodurene in the presence of stannic chloride yielded isodurylmesitylacetic acid, however. The treatment of isodurylacetic acid with an excess of mesitylene gave no mesitylacetic acid. Isodurylglycolic acid reacted normally with isodurene to form diisodurylacetic acid.

Isodurylmesitylketene was prepared from the acid by the action of thionyl chloride and a trace of pyridine. Reduction with *t*-butylmagnesium chloride yielded an isomer of 2-isoduryl-2-mesitylvinyl alcohol melting at 110-111°. The ketene also was treated successively with the Grignard reagent and acetyl chloride to give an acetate which when hydrolyzed yielded a second isomer of the alcohol melting at 92-93°.

The peroxide method also was applied to the synthesis of isodurylmesitylvinyl alcohol. The reaction of isoduralacetomesitylene with mesitylmagnesium bromide and of mesitalacetomesitylene with isodurylmagnesium bromide and subsequent treatment with oxygen yielded the same peroxide. Thermal decomposition of the peroxide was carried out in a number of ways, but in no case was a crystalline alcohol obtained. Treatment of the product with benzoyl chloride and pyridine gave a benzoate identical with that obtained from the isomer melting at 110-111°.

BIBLIOGRAPHY

1. Whitney, Thesis, Doctor of Philosophy, University of Illinois, 1944.
2. Fuson, Southwick and Rowland, J. Am. Chem. Soc., **66,** 1109 (1944).
3. Fuson, Rabjohn and Byers, **ibid., 66,** 1272 (1944).
4. Fuson, Armstrong, Wallace and Kneisley, **ibid., 66,** 1274 (1944).
5. Shenk, Thesis, Doctor of Philosophy, University of Illinois, 1944.
6. Rabjohn, Thesis, Doctor of Philosophy, University of Illinois, 1942.
7. L. J. Armstrong, Thesis, Doctor of Philosophy, University of Illinois, 1942.
8. Fuson, Lindsey and Welldon, J. Am. Chem. Soc., **64,** 2888 (1943).
9. Fuson and Soper, J. Org. Chem., **9,** 193 (1944).

VITA

The author was born in Providence, Rhode Island on March 18, 1920; attended the public schools of that city and was graduated from Central High School in June, 1937. He entered Brown University the following autumn and was granted a Bachelor of Science degree in June, 1941 and began graduate study at the University of Illinois the same year. From July, 1941 to June, 1943 he was employed at the Illinois State Geological Survey. The following year he was a special research assistant in chemistry. He was a teaching assistant during the summer of 1944 and held a University fellowship the next two semesters.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549820_0077